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(54) **PROCESS FOR PRODUCING ISOBUTENE POLYMER**

(57) The present invention provides a process for obtaining an isobutene polymer having a specified structure in a specific solvent system under industrially favorable conditions. The present invention relates to a process for the preparation of an isobutene polymer terminated by functional groups at a temperature of from not lower than -100°C to not higher than 0°C from the following components as essential components:

- (A) a cationically polymerizable monomer containing isobutene;
(B) an organic compound as an initiator/chain transfer agent represented by formula (1):



wherein X represents a halogen atom, an RO- group or an RCOO- group (in which R represents a monovalent organic group); R³ represents a polyvalent aromatic group or a substituted or unsubstituted polyvalent aliphatic hydrocarbon group; R¹ and R² may be the same or different and each represent a hydrogen atom or a substituted or unsubstituted monovalent hydrocarbon group, with the proviso that when R³ is a polyvalent aliphatic hydrocarbon group, one of R¹ and R² is not a hydrogen atom; and n represents an integer of from 1 to 6;

- (C) an aprotic solvent; and
(D) a Lewis acid,

wherein the component (C) exhibits a dielectric constant of from not less than 2.0 to not more than 5.5 at a temperature of 20°C.

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Description

TECHNICAL FIELD:

5 The present invention relates to a process for preparing an isobutene polymer. More particularly, the present invention relates to an advantageous process for preparing an isobutene polymer having functional groups at the terminals in the presence of an initiator.

The polymer prepared by the process disclosed herein exhibits excellent weathering resistance and gas barrier properties and good electrical insulating properties, and thus can be advantageously used as a starting material of
10 coating agent, sealing agent, sealing compound for electronic material, etc.

TECHNICAL BACKGROUND:

Among telechelic polymers, i.e., polymers having functional groups at a plurality of terminals, polymers having vinyl
15 groups at both terminals are useful as starting materials of photo-setting resins, ultraviolet(UV)-curing resins, electron radiation-curing resins, sealing compounds for electronics, adhesives, modifiers, coating materials, sealing compound for building, etc.

A functional group-terminated polymer (terminal functional polymers), e.g., isobutene polymer having a chlorine atom bonded to a tertiary carbon at both terminals has been known to be produced by an inifer process which comprises
20 the cationic polymerization of isobutene in the presence of 1,4-bis(α -chloroisopropyl)benzene (hereinafter, simply referred to as "p-DCC") as an initiator/chain transfer agent and boron trichloride as a catalyst (cf. U.S. Patent 4,276,394).

Further, many reports have been made by Kennedy et al., that when the foregoing cationic polymerization reaction is effected in a solvent containing a halogenated hydrocarbon (e.g., methyl chloride, methylene chloride) in the presence of an electron donor, an isobutene polymer having a small Mw/Mn value as determined by GPC, i.e., uniform molecular
25 weight can be obtained (Journal of Macromolecular Science Chemistry, A18 (1), 25 (1982), Polymer Bulletin, 20, 413 (1988), Polymer Bulletin, 26, 305 (1991), JP-A-1-318014 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"))).

The inventors made extensive studies of process for the production of an isobutene polymer by the foregoing inifer process on a commercial basis. In the course of the studies, the following problems were made clear.

30 (1) Since the polymerization reaction is normally effected at low temperatures, the solvent used exhibits a reduced dissolving power. Accordingly, when the monomer concentration is increased to enhance the yield, the resulting polymer separates out. Thus, the monomer concentration can hardly be enhanced. Referring to the process for the preparation of butyl rubber, etc., examples of the preparation process which comprises the precipitation of the result-
35 ing polymer have been reported. However, the precipitation of the polymer during the polymerization reaction must be avoided to reduce the molecular weight distribution of the polymer.

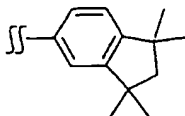
(2) The polymerization reaction rate is high. Therefore, when the monomer concentration is increased, the resulting heat generation during polymerisation makes it difficult to control the reaction temperature. If the rise in the reaction temperature is too great, undesirable side reactions such as proton-initiated reaction and chain transfer reaction
40 occur, increasing the molecular weight distribution (Mw/Mn) of the polymer and making it difficult to control the terminal functional groups. This disadvantageously produces a mixture of polymers having the following three terminal groups:

Chlorine terminal: $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{Cl}$

Isopropenyl terminal: $-\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$

45 Internal olefin terminal: $-\text{CH}=\text{C}(\text{CH}_3)_2$

In particular, if p-DCC is used, the rise in the monomer concentration gives a problem of subsidiary production of a large amount of an indanyl group having the following structure:



55 (3) Besides the effects on the properties of the polymer thus produced, the problem of toxicity caused by the use of a halogenic solvent arises. Most halogenated hydrocarbons are highly toxic. Halogenated hydrocarbons have

recently drawn attention from the standpoint of environmental pollution. Thus, the exhaust of halogenated hydrocarbons out of the system is now under severe regulation. The use of a halogenated hydrocarbon which has heretofore been used in the polymerization reaction, such as methylene chloride and methyl chloride presents problems of deactivation of the catalyst after the polymerization reaction and disposal of waste water or waste solvent containing halogenated hydrocarbon generated at the rinsing step. In order to satisfy the regulation on exhaust, large scale facilities and high disposal cost are required. The regulation will likely be severer in the future, requiring further countermeasures.

It has been widely known that when the temperature of the polymerization reaction is raised, carbocations at the growth terminal become instable, causing side reactions such as chain transfer and production of indanyl group (J.P. Kennedy, E. Marechal, Carbocationic Polymerization, John Wiley & Sons (1982)).

The rise in the monomer concentration gives a greater rise in the temperature of the polymerization reaction. Therefore, the monomer concentration used in examples which have been reported is low and normally not more than 1 mol/l (Polym. Bull., 21, 5 (1989), Polym. Bull., 21, 125 (1989), Polym. Bull., 21, 273 (1989), Polym. Bull., 21, 293 (1989), Polym. Bull., 26, 305 (1991), Polym. Bull., 29, 239 (1992)).

However, from the industrial viewpoint, it has been keenly desired to raise the weight of polymer which can be produced per unit volume.

Since carbocations as growth seeds must be stable in the polymerization of isobutene in a living cation system, it has heretofore been considered preferred to effect the reaction in a solvent having some polarity at a temperature low enough to allow cations to be present in a relatively stable state. An isobutene polymer exhibits a low solubility in a polar solvent such as methyl chloride and methylene chloride at low temperatures. Thus, a hydrocarbon solvent may be incorporated in the polar solvent to increase the solubility of the isobutene polymer in the polar solvent. However, a report was made that the use of a mixture of methyl chloride and hexane wherein the proportion of hexane is not less than 40% causes chain transfer which appears in the form of two peaks on GPC chart (bimodal) (Polym. Bull., 21, 273 (1989)). The phenomenon that two peaks appear on GPC chart demonstrates the rise in the molecular weight distribution and is thus undesirable.

Further, JP-A-3-174403, JP-A-3-287605, and U.S. Patents 4,327,201 and 5,169,914 disclose that as a polymerization solvent there may be used an aliphatic organic solvent such as butane, pentane, hexane and heptane, aromatic organic solvent such as benzene, toluene and xylene, nitro compound such as nitromethane and nitroethane, halogenated organic solvent or mixture thereof without any restriction so far as it exerts no adverse effects on the polymerization activity of the initiator.

However, the examples in these patents merely give examples of a mixture of methylene chloride and hexane having a high polarity. Further, the resulting isobutene polymer contains a large number of indanyl groups as by-products. Thus, desirable polymers cannot be obtained. Moreover, as described in the comparative examples of the present application, the polymerization in the presence of hexane, which has a low polarity, produces an isobutene polymer having a molecular weight distribution (M_w/M_n) as extremely high as 7.02 and a large number of indanyl groups. It has thus been made clear that the foregoing polymerization process is not desirable.

An object of the present invention is to solve the foregoing problems and thus provide a process for the preparation of an industrially favorable isobutene polymer.

DISCLOSURE OF THE INVENTION:

The inventors found that the conventional problems can be solved by the use of a solvent having a specified dielectric constant. The inventors also found that the use of such a solvent makes it possible to obtain the desired isobutene polymer having a small molecular weight distribution without using the halogenated hydrocarbon which has heretofore been used. If no halogenated hydrocarbons are used, there arises no problem of the discharge of halogenated hydrocarbons. This advantageously provides a drastic reduction of facilities and cost required for disposal of waste water, making it possible to solve the foregoing problems (1) to (3) at once. However, whether or not such a halogenated hydrocarbon is present has no specific effects on the properties of the resulting polymer. Even if a solvent containing a halogenated hydrocarbon is used, when the content of halogenated hydrocarbon is reduced to lower the polarity of the solvent, the foregoing problems (1) and (2) can be solved.

The present invention has the following constitutions:

1. A process for preparing an isobutene polymer having functional groups at the terminals at a temperature of from not lower than -100°C to not higher than 0°C from the following components as essential components:

(A) a cationic polymerizable monomer containing isobutene;

(B) an organic compound as an initiator/chain transfer agent represented by formula (1):



wherein X represents a halogen atom, an RO- group or an RCOO- group (in which R represents a monovalent organic group); R³ represents a polyvalent aromatic group or a substituted or unsubstituted polyvalent aliphatic hydrocarbon group; R¹ and R² may be the same or different and each represent a hydrogen atom or a substituted or unsubstituted monovalent hydrocarbon group, with the proviso that when R³ is a polyvalent aliphatic hydrocarbon group, one of R¹ and R² is not a hydrogen atom; and n represents an integer of from 1 to 6;

(C) an aprotic solvent free of halogenated hydrocarbon; and

(D) a Lewis acid,

wherein the component (C) exhibits a dielectric constant of from not less than 2.0 to not more than 4.0 at a temperature of 20°C.

2. A process for preparing an isobutene polymer having functional groups at the terminals at a temperature of from not lower than -100°C to not higher than 0°C from the following components as essential components:

(A) a cationic polymerizable monomer containing isobutene;

(B) an organic compound as an initiator/chain transfer agent represented by formula (1):



wherein X represents a halogen atom, an RO- group or an RCOO- group (in which R represents a monovalent organic group); R³ represents a polyvalent aromatic group or a substituted or unsubstituted polyvalent aliphatic hydrocarbon group; R¹ and R² may be the same or different and each represent a hydrogen atom or a substituted or unsubstituted monovalent hydrocarbon group, with the proviso that when R³ is a polyvalent aliphatic hydrocarbon group, one of R¹ and R² is not a hydrogen atom; and n represents an integer of from 1 to 6;

(C) an aprotic solvent containing halogenated hydrocarbon; and

(D) a Lewis acid,

wherein the component (C) exhibits a dielectric constant of from not less than 3.5 to not more than 5.5 at a temperature of 20°C.

3. The process for preparing an isobutene polymer terminated by functional groups according to the above 1 or 2, wherein the component (C) contains an aromatic hydrocarbon.

4. The process for preparing an isobutene polymer terminated by functional groups according to any one of the above 1 to 3, wherein the component (C) is a mixture of an aromatic hydrocarbon and an aliphatic hydrocarbon.

5. The process for preparing an isobutene polymer terminated by functional groups according to any one of the above 1, 3 and 4, wherein the component (C) exhibits a dielectric constant of from not less than 2.0 to not more than 2.5 at a temperature of 20°C.

6. The process for preparing an isobutene polymer terminated by functional groups according to any one of the above 3 to 5, wherein the aromatic hydrocarbon is selected from the group consisting of benzene, toluene, xylene and ethylbenzene.

7. The process for preparing an isobutene polymer terminated by functional groups according to any one of the above 1 to 6, wherein the concentration of the component (A) in the system is from 5 to 40 wt%.

8. The process for preparing an isobutene polymer terminated by functional groups according to any one of the above 1 to 7, wherein the component (B) is selected from the group consisting of p-dicumyl chloride, m-dicumyl chloride, p-dicumyl methoxide, m-dicumyl methoxide, 1,3,5-tricumyl chloride and 1,3,5-tricumyl methoxide.

9. The process for preparing an isobutene polymer terminated by functional groups according to any one of the above 1 to 8, wherein the component (D) is boron trichloride or titanium tetrachloride.

10. The process for preparing an isobutene polymer terminated by functional groups according to any one of the above 1 to 9, wherein an electron donor is further added as a component (E) in addition to the components (A) to (D).

11. A process for preparing an isobutene polymer having carbon-carbon double bonds at the terminals, which comprises adding an allyl trimethylsilane in an amount of from 0.5 to 1.5 mol per mol of the group X in the component (B) before the formation of an isobutene polymer terminated by functional groups according to any one of the above 1 to 10 or before the deactivation of the component (D) following the formation of the isobutene polymer.

12. A process for preparing an isobutene polymer having carbon-carbon double bonds at the terminals, which comprises adding 1,9-decadiene in an amount of from 1.5 to 10.0 mol per mol of the group X in the component (B) before the formation of an isobutene polymer terminated by functional groups according to any one of the above 1 to 10 or before the deactivation of the component (D) following the formation of the isobutene polymer.

In the present invention, the number-average molecular weight (M_n) of the isobutene polymer is usually from 500 to 300,000, preferably from 1,000 to 50,000. If M_n is smaller than 500, the excellent characteristics inherent to isobutene polymers are lost. On the contrary, if M_n exceeds 300,000, the resulting polymer is solid, extremely deteriorating its workability. The number-average molecular weight (M_n) and M_w/M_n value of the isobutene polymer were determined by GPC using a polystyrene gel column (Shodex K-804, manufactured by Showa Denko K.K.; mobile phase: chloroform) in polystyrene equivalence.

The term "cationic polymerizable monomer containing isobutene" as used herein is not limited to a monomer made only of isobutene but is meant to include a monomer the isobutene component of which is substituted by a cationic polymerizable monomer copolymerizable with isobutene in a proportion of not more than 50% by weight (hereinafter, simply referred to as "%").

Examples of the cationic polymerizable monomer copolymerizable with isobutene include olefins having 3 to 12 carbon atoms, conjugated dienes, vinyl ethers, aromatic vinyl compounds, norbornenes, and vinyl silanes. Preferred among these cationic polymerizable monomers are olefins having 3 to 12 carbon atoms and aromatic vinyl compounds.

Specific examples of the cationic polymerizable monomer copolymerizable with isobutene usually include propene, 1-butene, 2-butene, 2-methyl-1-butene, 3-methyl-1-butene, pentene, hexene, cyclohexene, vinyl cyclohexane, 5-ethylidenenorbornene, 5-propylenenorbornene, butadiene, isoprene, cyclopentadiene, methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether, vinyl carbazole, methoxystyrene, ethoxystyrene, t-butoxystyrene, hexenyloxystyrene, styrene, α -methylstyrene, methylstyrene, dimethylstyrene, chloromethylstyrene, chlorostyrene, indene, β -pinene, vinyltrichlorosilane, vinylmethylchlorosilane, vinyl dimethylchlorosilane, vinyl dimethylmethoxysilane, vinyltrimethylsilane, divinyl-dichlorosilane, divinyl dimethoxysilane, divinyl dimethylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, trivinylmethylsilane, γ -methacryloyloxypropyltrimethoxysilane, and γ -methacryloyloxypropylmethyl dimethoxysilane.

Preferred among these cationic polymerizable monomers are propene, 1-butene, 2-butene, cyclopentadiene, 5-ethylidenenorbornene, isobutyl vinyl ether, methoxystyrene, and styrene. One of these cationic polymerizable monomers copolymerizable with isobutene may be used in combination with isobutene. Two or more of these cationic polymerizable monomers may be used in combination.

In the present invention, the monomer concentration during polymerization is normally from 1 to 75 wt%, preferably from 5 to 60 wt%, more preferably from 10 to 40 wt%, most preferably from 15 to 30 wt%. If the monomer concentration is less than 1 wt%, the production efficiency is disadvantageously reduced, though causing no troubles on the polymerization itself. If the monomer concentration exceeds 75 wt%, the polymerization system is a precipitation system, making it impossible to obtain a good polymer.

Examples of the compound represented by the foregoing formula (1) of the present invention include a compound represented by formula (2):



(2)

wherein A represents a group having 1 to 4 aromatic rings; Y represents a group represented by formula (3):



(in which R⁶ and R⁷ may be the same or different and each represent a hydrogen atom or a monovalent hydrocarbon group having 1 to 20 carbon atoms; X represents a halogen atom, an R⁴COO- group (R⁴ represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms) or an R⁵O- group (R⁵ represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms)); and n represents an integer of from 1 to 8; a compound represented by formula (4):



wherein B represents a substituted or unsubstituted hydrocarbon group having 4 to 40 carbon atoms; Z represents a halogen atom bonded to tertiary carbon atom, an R⁸COO- group (in which R⁸ represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms) or an R⁹O- group (in which R⁹ represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms); and m represents an integer of from 1 to 4; and an oligomer having α -halostyrene units. However, the present invention is not limited to these compounds. These compounds may be used singly or in combination.

In the compound represented by the formula (2), the group A having 1 to 4 aromatic rings may be either one produced by a condensation reaction or may be an uncondensed product. Examples of the group containing aromatic rings include phenyl, biphenyl, naphthyl, anthryl, phenanthryl, pyrenyl, di- to pentavalent groups derived from these groups, and mono- to hexavalent groups derived from Ph-(CH₂)_l-Ph (in which Ph represents a phenyl group, and l represents an integer of from 1 to 10). These groups having aromatic rings may be substituted by straight-chain and/or branched aliphatic hydrocarbon groups having 1 to 20 carbon atoms or groups containing a functional group such as hydroxyl group, ether group and vinyl group.

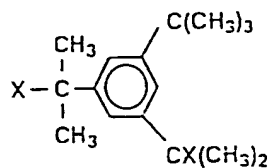
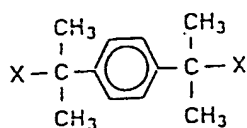
As the compound represented by the formula (4), there may also be used one having a functional group other than Z, such as vinyl group and silyl group.

Examples of the oligomer having an α -halostyrene unit, which can be used as the initiator/chain transfer agent, include oligomers of α -chlorostyrene, and oligomers obtained by the copolymerization of α -chlorostyrene with a monomer copolymerizable therewith.

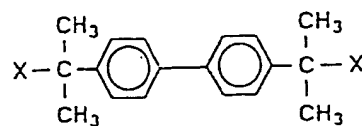
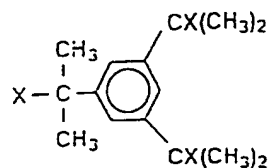
In the present invention, the use of a compound having two or more halogen atoms, R⁴COO- groups (in which R⁴ represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms) or R⁵O- groups (in which R⁵ represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms) or a compound having a halogen atom, an R⁴COO- group or an R⁵O- group and other reactive functional groups, from among the compounds represented by the formula (1), as an initiator/chain transfer agent, can advantageously provide the resulting polymer with a higher functionality.

Specific examples of the compound represented by the foregoing formula (1), which can be usually employed, include the following compounds:

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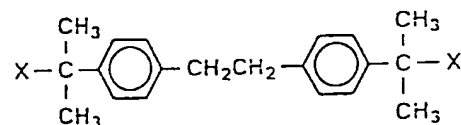
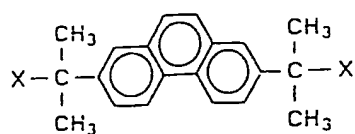


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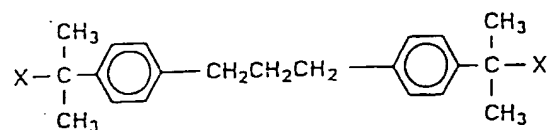
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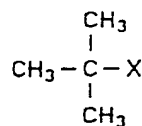
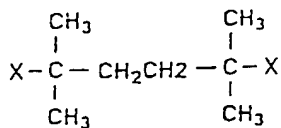


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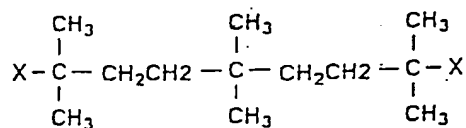
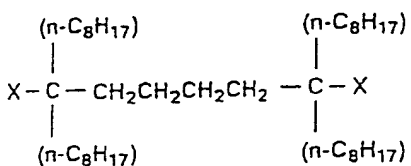


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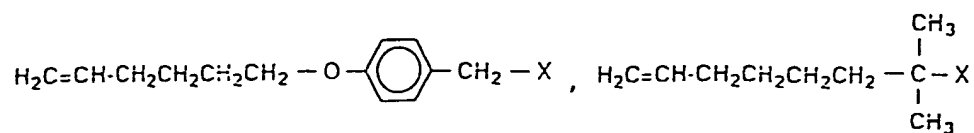
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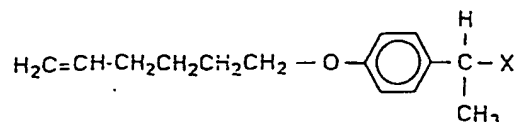


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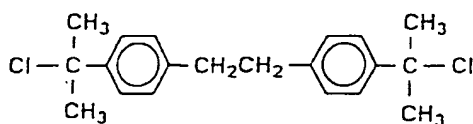
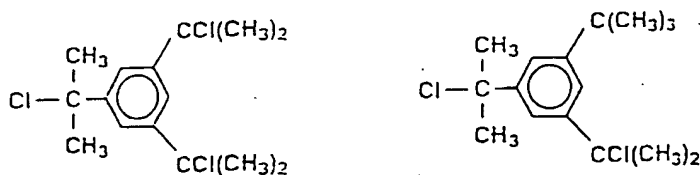
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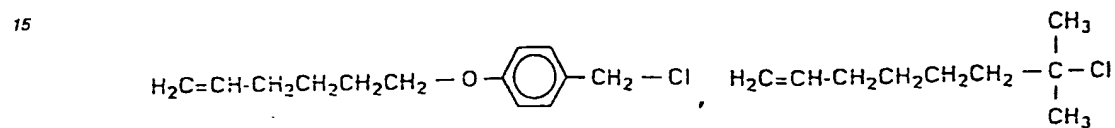
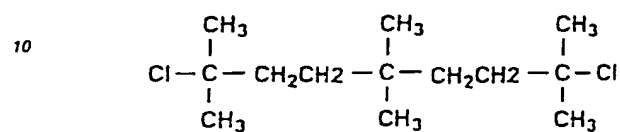
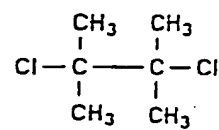
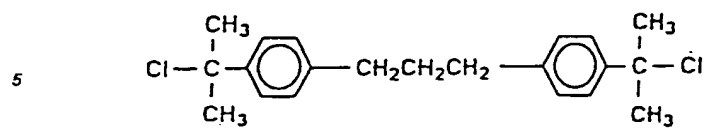


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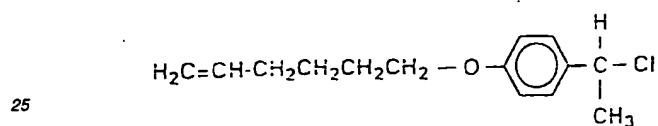


15 wherein X represents a halogen atom, an $\text{R}^4\text{COO}-$ group (in which R^4 represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms) or an $\text{R}^5\text{O}-$ group (in which R^5 represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms); and
 20 oligomer of α -chlorostyrene. However, the present invention is not limited to these compounds. Preferred among these compounds are compounds such as

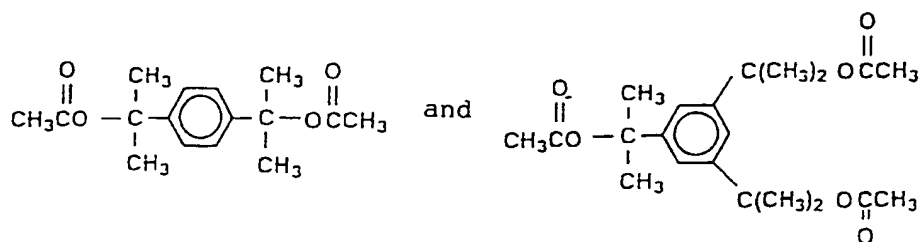
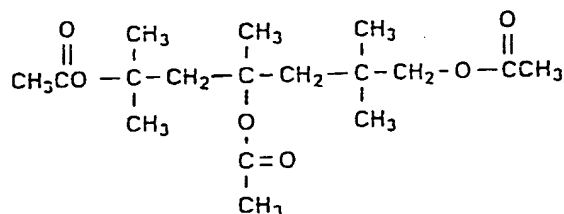
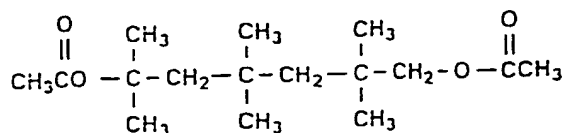




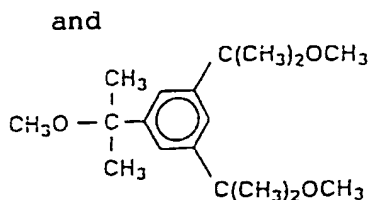
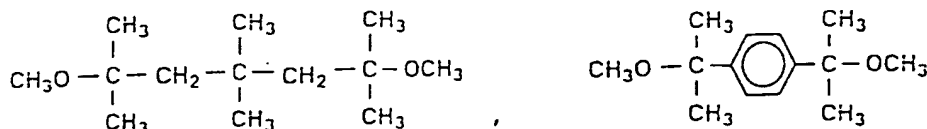
20 and



CH₃COO- group-containing compounds such as



and CH₃O- group-containing compounds such as



These compounds are components which are used as initiators/chain transfer agents. These compounds may be used singly or in admixture in the present invention. By controlling the amount of these compounds to be used, the number-average molecular weight of the resulting isobutene polymer can be arbitrarily predetermined.

In the present invention, the amount of the compound represented by the foregoing formula (1) to be used is usually from 0.01 to 20% by weight, preferably from 0.1 to 10% by weight based on the weight of the cationic polymerizable monomer containing isobutene.

As the Lewis acid which can be used in the present invention, there may be used any known metal complex without any restriction. In general, TiCl_4 , BCl_3 , SnCl_4 , AlCl_3 , $\text{CH}_3\text{CH}_2\text{AlCl}_2$, $(\text{CH}_3\text{CH}_2)_2\text{AlCl}$, VCl_5 , FeCl_3 , BF_3 , etc. may be used. However, the present invention is not limited to these compounds. Preferred among these Lewis acids are TiCl_4 and BCl_3 .

In the present invention, the Lewis acid is usually used in an amount of from 0.1 to 100% by weight, preferably from 1 to 30% by weight based on the weight of the cationic polymerizable monomer containing isobutene. If the amount of the Lewis acid to be used as a catalyst component falls below 0.1% by weight, a problem arises that the yield of the product of the cationic polymerization reaction is reduced. On the contrary, if the amount of the Lewis acid exceeds 100% by weight, no merits can be obtained.

In the present invention, the aprotic solvent free of halogenated hydrocarbon, if used as a polymerization solvent, should have a dielectric constant of from not less than 2.0 to not more than 4.0 at a temperature of 20°C. If the dielectric constant of the solvent falls below 2, a good isobutene polymer could not be obtained. (Therefore, pentane, hexane, etc. cannot be used as single solvent.)

Examples of the aprotic solvent free of halogenated hydrocarbon to be used as a polymerization solvent include butane, pentane, neopentane, hexane, cyclohexane, methylcyclohexane, ethylcyclohexane, heptane, octane, benzene, toluene, xylene, and ethylbenzene. Preferred among these aprotic solvents are toluene, hexane, and heptane.

Examples of the mixed solvent (mixing ratio (vol/vol)) include various combinations such as toluene/hexane (5/5 to 10/0), toluene/heptane (5/5 to 10/0), toluene/methylcyclohexane (5/5 to 10/0) and toluene/ethylcyclohexane (5/5 to 10/0). One of unexpected merits which have been made obvious in the course of the study in the present invention is the fact that the use of a solvent free of halogenated hydrocarbon makes it possible to obtain a good isobutene polymer even if the dielectric constant of the solvent is low. A low dielectric constant system tends to show a small temperature rise during polymerization reaction. Therefore, the problem of heat removal accompanied by scaling up the reaction can be easily solved.

In the present invention, the aprotic solvent containing halogenated hydrocarbon, if used as a polymerization solvent, should have a dielectric constant of from not less than 3.5 to not more than 5.5 at a temperature of 20°C.

Specific examples of the aprotic solvent containing halogenated hydrocarbon to be used as a polymerization solvent include a mixture of halogenated hydrocarbon such as methyl chloride, methylene chloride, 1,2-dichloroethane, 1,1-dichloroethane and chlorination product of propane, butane and pentane and hydrocarbon such as butane, pentane, neopentane, hexane, cyclohexane, methylcyclohexane, ethylcyclohexane, heptane, octane, benzene, toluene and xylene. Examples of the mixed solvent (mixing ratio (vol/vol)) include various combinations such as methylene chloride/hexane (4/6 to 8/2), methyl chloride/hexane (2/8 to 1/9), and methylene chloride/heptane (4/6 to 8/2). Heretofore, if a solvent containing halogenated hydrocarbon is used, the polymerization has been often effected in a solvent system having a dielectric constant of not less than 6. In the present invention, by reducing the dielectric constant of the solvent, the polymerization rate can be controlled, making it possible to control the temperature rise during polymerization.

In the present invention, the dielectric constant of the mixed solvent system can be approximately calculated by determining the additive mean (arithmetic mean) of the dielectric constant of the constituents over the mixing ratio of the constituents on a weight-average basis. The dielectric constant (typical value) of various solvents used for the calculation of the dielectric constant of the mixed solvent will be listed below.

Toluene: 2.24; ethylbenzene: 2.40; o-xylene: 2.27; m-xylene: 2.37; n-pentane: 1.84; n-hexane: 1.89; n-heptane: 1.92; methylcyclohexane: 2.02; methylene chloride: 7.77; methyl chloride: 12.9

In the present invention, the polymerization solvent is preferably free of halogenated hydrocarbon for the reason that waste water disposal facilities can be simplified. The term "solvent free of halogenated hydrocarbon" as used in the present application is meant to indicate a solvent which may contain halogenated hydrocarbon to an extent such that no special treatments for halogenated hydrocarbon in waste water or waste solvent generated from the catalyst deactivation and rinsing process after polymerization reaction are required.

In the present invention, an electron donor is preferably used as the component (E) to control side reactions more efficiently. As the electron donor component there may be widely used any known electron donor components having a donor number of from 15 to 50. Preferred examples of such electron donor components include pyridines, amines, amides, and sulfoxides.

Specific examples of the electron donor component usually include 2,6-di-t-butylpyridine, 2-t-butylpyridine, 2,4,6-trimethylpyridine, 2,6-dimethylpyridine, 2-methylpyridine, pyridine, diethylamine, trimethylamine, triethylamine, tributylamine, diethylamine, N,N-dimethylaniline, N,N-dimethylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, dimethylsulfoxide, diethyl ether, methyl acetate, ethyl acetate, trimethyl phosphate, and triamide hexamethylphosphate. Preferred among these electron donor components are 2,6-di-t-butylpyridine, 2,6-dimethylpyridine, 2-methylpyridine, pyridine, diethylamine, trimethylamine, triethylamine, N,N-dimethylformamide, N,N-dimethylacetamide, and dimethylsulfoxide. Picolines are further preferred. Particularly preferred of these electron donors is α -picoline (2-methylpyridine), which can exert a remarkable effect despite of its small donor number.

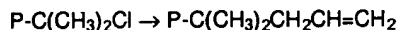
In the present invention, the electron donor component is usually used in an amount of from 0.01 to 10 mol, preferably from 0.1 to 2 mol per mol of the group X in the compound represented by the general formula (1).

In the present invention, the polymerization reaction is not specifically limited and can be accomplished by any conventional polymerization method. Among the foregoing components, i.e., (A) cationic polymerizable monomer containing isobutene and (D) Lewis acid, a solution containing (D) a Lewis acid may be added to a solution of (A) a cationic polymerizable monomer containing isobutene in a batch process. Alternatively, a solution of (A) a cationic polymerizable monomer containing isobutylene may be continuously added to a solution containing (D) a Lewis acid in a semi-batch process. Further, a continuous process may be employed which comprises continuously charging all the foregoing components into the reaction system while withdrawing the reaction product.

In the present invention, the polymerization reaction can be followed by a substitution reaction or addition reaction on the functional terminal groups formed at the terminals of the polymer to produce an isobutene polymer having carbon-carbon double bonds at the terminals. In other words, the reaction of the resulting isobutene polymer, preferably at tertiary chlorine group end, with a specific end capping agent makes it easy to obtain a polymer having carbon-carbon double bonds at the terminals. In general, the functional terminal group is chiefly a tertiary halogen group. However, the foregoing isopropenyl group or internal olefin group may be included.

For example, in the conversion of chlorine group end to carbon-carbon double bond end by the substitution reaction using an allyl trimethylsilane, the desired carbon-carbon double bond end can be easily produced only by adding a required amount of an allyl trimethylsilane before the deactivation of the component (D). The reaction temperature is preferably as low as the polymerization temperature. Since the substitution reaction proceeds at a high rate at low temperatures, it is usually completed in 30 minutes. The amount of the allyl trimethylsilane to be used may be from 1.0 to 1.5 mol per mol of the group X in the component (B). If it is necessary to obtain a polymer having a small content of carbon-carbon double bonds, the amount of the allyl trimethylsilane added may be not more than 1 mol per mol of the group X. Since the allyl trimethylsilane doesn't take part in the polymerization reaction, it may be added to the reaction system before polymerization.

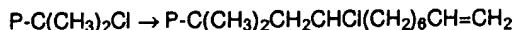
[Reaction scheme]



wherein P represents a polymer residue.

Further, in the conversion of chlorine group end to carbon-carbon double bond end by the addition reaction using a non-conjugated diene such as 1,9-decadiene, the desired carbon-carbon double bond end can be easily produced only by adding a required amount of a non-conjugated diene before the deactivation of the component (D) as in the case where an allyl trimethylsilane is used. The addition reaction temperature is preferably as low as the polymerization temperature. The addition reaction at low temperatures is usually completed in about 6 hours. The amount of the non-conjugated diene to be used may be from 1.5 to 10.0 mol per mol of the group X in the component (B). If it is necessary to obtain a polymer having a small carbon-carbon double bond content, the reaction time may be reduced. Alternatively, the amount of 1,9-decadiene added may be not more than 1 mol per mol of the group X. In this system, a Lewis acid as the component (D) may be added, or the reaction temperature may be further lowered for the purpose of further accelerating the addition reaction.

[Reaction scheme]



wherein P represents a polymer residue.

BEST MODE FOR CARRYING THE INVENTION:

The present invention will be further described in the following examples, but the present invention should not be construed as being limited thereto.

Example 1:

In a reaction vessel were charged 276 ml of toluene, 112 ml of an isobutene monomer, 1.156 g of p-DCC and 0.186 g of α -picoline. The reaction mixture was then stirred with the reaction vessel being surrounded by a dry ice-ethanol bath so that it was cooled to a temperature of -70°C . A mixture of 3.95 ml of TiCl_4 and 4 ml of toluene was then added to the reaction system to initiate reaction. After the completion of the reaction, the reaction solution was poured into a large amount of water with stirring so that it was washed. The resulting organic phase and aqueous phase were then separated from each other to remove the catalyst. The organic phase was then subjected to evaporation under reduced

pressure to remove the volatile content. Thus, an isobutene polymer was obtained. The reaction conditions used and the properties of the polymer thus obtained are shown in Tables 1 and 2 below.

Example 2:

The air in a 500-ml four-necked flask with a three-way cock was replaced by nitrogen. Into the vessel were charged 280 ml of toluene (which had been allowed to stand with molecular sieves 3A overnight or longer so that it was dried) and 2.31 g (10 mmol) of p-DCC through a syringe. To the three-way cock was then connected a pressure glass liquefied gas thief tube equipped with a needle valve in which 112 ml of an isobutene monomer had been charged. The polymerization vessel was then dipped in a -60°C dry ice/ethanol bath so that it was cooled. The system in the vessel was then evacuated by a vacuum pump. The needle valve was then opened so that the isobutene monomer was introduced from the liquefied gas thief tube into the polymerization vessel. Nitrogen gas was then introduced into the polymerization vessel from one of the three ways of the cock so that the pressure of the vessel was returned to normal value (atmospheric pressure). 0.186 g (2 mmol) of 2-methylpyridine was then charged into the polymerization vessel. 2.74 ml (25 mmol) of titanium tetrachloride was then added to the -60°C monomer solution to initiate polymerization. When 60 minutes passed since the initiation of the reaction, 3.42 g (30 mmol) of an allyl trimethylsilane was added to the reaction mixture. The reaction mixture was further allowed to undergo reaction at a temperature of -60°C for 120 minutes. The reaction solution was then washed with 200 ml of water four times. The solvent was then evaporated to obtain an isobutene polymer. The reaction conditions used and the properties of the resulting polymer are altogether shown in Table 1.

Example 3:

The air in a 300-ml four-necked flask with a three-way cock was replaced by nitrogen. Into the vessel were charged 112 ml of toluene (which had been allowed to stand with molecular sieves 3A overnight or longer so that it was dried), 49 ml of heptane (which had been allowed to stand with molecular sieves 3A overnight or longer so that it was dried), 1.16 g (5.0 mmol) of p-DCC and 0.093 g (1 mmol) of 2-methylpyridine through a syringe. To the three-way cock was then connected a pressure glass liquefied gas thief tube equipped with a needle valve in which 56 ml of an isobutene monomer had been charged. The polymerization vessel was then dipped in a -70°C dry ice/ethanol bath so that it was cooled. The system in the vessel was then evacuated by a vacuum pump. The needle valve was then opened so that the isobutene monomer was introduced from the liquefied gas thief tube into the polymerization vessel. Nitrogen gas was then introduced into the polymerization vessel from one of the three ways of the cock so that the pressure of the vessel was returned to normal value. 1.64 ml (15 mmol) of titanium tetrachloride was then added to the monomer solution to initiate polymerization. When 90 minutes passed since the initiation of the reaction, 1.15 g (10 mmol) of an allyl trimethylsilane was added to the reaction mixture. The reaction mixture was further allowed to undergo reaction at a temperature of -70°C for 90 minutes. The reaction solution was then washed with 200 ml of water four times. The solvent was then evaporated to obtain an isobutene polymer. The reaction conditions used and the properties of the resulting polymer are altogether shown in Tables 1 and 2.

Example 4:

An isobutene polymer was produced in the same manner as in Example 3 except that 128 ml of toluene and 32 ml of heptane were used as solvents. The isobutene polymer thus produced was then evaluated in the same manner as in Example 3. The reaction conditions used and the properties of the resulting polymer are altogether shown in Tables 1 and 2.

Example 5:

The air in a 500-ml four-necked flask with a three-way cock was replaced by nitrogen. Into the vessel were charged 255 ml of toluene (which had been allowed to stand with molecular sieves 3A overnight or longer so that it was dried), 112 ml of hexane (which had been allowed to stand with molecular sieves 3A overnight or longer so that it was dried) and 1.16 g (5.0 mmol) of p-DCC through a syringe. To the three-way cock was then connected a pressure glass liquefied gas thief tube equipped with a needle valve in which 112 ml of an isobutene monomer had been charged. The polymerization vessel was then dipped in a -70°C dry ice/ethanol bath so that it was cooled. The system in the vessel was then evacuated by a vacuum pump. The needle valve was then opened so that the isobutene monomer was introduced from the liquefied gas thief tube into the polymerization vessel. Nitrogen gas was then introduced into the polymerization vessel from one of the three ways of the cock so that the pressure of the vessel was returned to normal value. 0.186 g (2 mmol) of 2-methylpyridine was then added to the reaction system. 7 ml of a toluene solution of 2.76 ml (25 mmol) of titanium tetrachloride was then added to the reaction system to initiate polymerization. When the reaction was initiated, the temperature rise was 8.5°C. When 2 hours passed since the initiation of the reaction, 5.48 ml (50 mmol) of titanium

tetrachloride and 13.83 g (100 mmol) of 1,9-decadiene were added to the reaction system. When 6 hours passed since the addition of 1,9-decadiene, the reaction solution was washed with 500 ml of water four times. The solvent was evaporated. The resulting isobutene polymer was then dissolved in a small amount of hexane. 1,000 ml of acetone was then added to the reaction solution with stirring so that the polymer separated out by the precipitation. The polymer thus obtained was dissolved in hexane. The volatile content was then evaporated to obtain an isobutene polymer. The reaction conditions used and the properties of the resulting polymer are altogether shown in Tables 1 and 2.

Example 6:

The air in a 500-ml four-necked flask with a three-way cock was replaced by nitrogen. Into the vessel were charged 126 ml of toluene (which had been allowed to stand with molecular sieves 3A overnight or longer so that it was dried), 54 ml of methylcyclohexane (which had been allowed to stand with molecular sieves 3A overnight or longer so that it was dried) and 1.16 g (5.0 mmol) of p-DCC through a syringe. To the three-way cock was then connected a pressure glass liquefied gas thief tube equipped with a needle valve in which 56 ml of an isobutene monomer had been charged. The polymerization vessel was then dipped in a -70°C dry ice/ethanol bath so that it was cooled. The system in the vessel was then evacuated by a vacuum pump. The needle valve was then opened so that the isobutene monomer was introduced from the liquefied gas thief tube into the polymerization vessel. Nitrogen gas was then introduced into the polymerization vessel from one of the three ways of the cock so that the pressure of the vessel was returned to normal value. 0.093 g (1 mmol) of 2-methylpyridine was then added to the reaction system. 1.65 ml (15.1 mmol) of titanium tetrachloride was then added to the reaction system to initiate polymerization.

When 70 minutes passed since the initiation of the reaction, 1.24 g (10.8 mmol) of an allyl trimethylsilane was added to the reaction system. The reaction system was further allowed to undergo reaction at a temperature of -70°C for 90 minutes. The reaction solution was then washed with 400 ml of water four times. The solvent was evaporated. The resulting isobutene polymer was then dissolved in a small amount of hexane. 500 ml of acetone was then added to the solution with stirring so that the polymer separated out by the precipitation. The polymer thus obtained was dissolved in hexane. The volatile content was then evaporated to obtain an isobutene polymer. The reaction conditions used and the properties of the resulting polymer are altogether shown in Tables 1 and 2.

Example 7:

An isobutene polymer was produced in the same manner as in Example 1 except that 28 ml of an isobutene monomer, 0.289 g of p-DCC and 0.047 g of α -picoline were charged into the reaction system. The isobutene polymer thus produced was then evaluated in the same manner as in Example 1. The reaction conditions used and the properties of the polymer thus obtained are altogether shown in Tables 1 and 2. The maximum temperature rise during reaction was 5°C.

Example 8:

An isobutene polymer was produced in the same manner as in Example 7 except that the polymerization temperature was -50°C. The isobutene polymer thus produced was then evaluated in the same manner as in Example 7. The reaction conditions used and the properties of the resulting polymer are altogether shown in Tables 1 and 2.

Example 9:

An isobutene polymer was produced in the same manner as in Example 7 except that 248 ml of toluene and 28 ml of hexane were charged into the reaction vessel. The isobutene polymer thus produced was then evaluated in the same manner as in Example 7. The reaction conditions used and the properties of the polymer thus obtained are altogether shown in Tables 1 and 2.

Comparative Example 1:

Into a reaction vessel were charged 276 ml of hexane, 28 ml of an isobutene monomer, 0.289 g of p-DCC and 0.047 g of α -picoline. The reaction mixture was then stirred with the reaction vessel being surrounded by a dry ice-ethanol bath so that it was cooled to a temperature of -70°C. A mixture of 7.9 ml of TiCl_4 and 4 ml of hexane was then added to the reaction system to initiate reaction. After the completion of the reaction, the reaction solution was poured into a large amount of water with stirring so that it was washed. The resulting organic phase and aqueous phase were then separated from each other to remove the catalyst. The organic phase was then subjected to evaporation under reduced pressure to remove the volatile content. Thus, an isobutene polymer was obtained. The reaction conditions used and the properties of the polymer thus obtained are altogether shown in Tables 1 and 2 below.

Example 10:

Into a reaction vessel were charged 76 ml of methane dichloride, 196 ml of hexane, 28 ml of an isobutene monomer, 0.289 g of p-DCC and 0.047 g of α -picoline. The reaction mixture was then stirred with the reaction vessel being surrounded by a dry ice-ethanol bath so that it was cooled to a temperature of -70°C. A mixture of 3.95 ml of TiCl₄ and 8 ml of methane dichloride was then added to the reaction system to initiate reaction. After the completion of the reaction, the reaction solution was poured into a large amount of water with stirring so that it was washed. The resulting organic phase and aqueous phase were then separated from each other to remove the catalyst. The organic phase was then subjected to evaporation under reduced pressure to remove the volatile content. Thus, a polymer product was obtained. The reaction conditions used and the properties of the polymer thus obtained are altogether shown in Tables 1 and 2 below.

Example 11:

Into a reaction vessel were charged 56 ml of methane dichloride and 216 ml of hexane. The other reaction conditions were the same as used in Example 10. A solution of 3.95 ml of a catalyst in 8 ml of hexane was then poured into the reaction vessel to initiate reaction. Thus, a polymer product was obtained. The reaction conditions used and the properties of the resulting polymer are altogether shown in Tables 1 and 2 below. The maximum temperature rise during reaction was 7°C.

Example 12:

A reaction was effected in the same manner as in Example 10 except that 104 ml of methane dichloride and 168 ml of hexane were charged into the reaction vessel. Thus, a polymer product was obtained. During the reaction, 9.95 g of 1,9-decadiene was added to the reaction system to introduce a functional group into the polymer. The reaction temperature was -50°C. The reaction conditions used and the properties of the resulting polymer are altogether shown in Tables 1 and 2 below.

The molecular weight of the polymer product and its distribution were measured by GPC analysis. As a result, no low molecular by-products were detected. The maximum temperature rise during reaction was 7°C.

Comparative Example 2:

Into a reaction vessel were charged 28 ml of methane dichloride and 244 ml of hexane. The other conditions were the same as used in Example 10. A solution of 3.95 ml of a catalyst in 8 ml of hexane was then poured into the reaction vessel to initiate reaction. Thus, a polymer product was obtained. The reaction conditions used and the properties of the resulting polymer are altogether shown in Tables 1 and 2 below.

Comparative Example 3:

A reaction was effected in the same manner as in Example 12 except that 160 ml of methane dichloride, 112 ml of hexane and 0.578 g of p-DCC were charged into the reaction vessel. Thus, a polymer product was obtained. The reaction conditions used and the properties of the resulting polymer are altogether shown in Tables 1 and 2 below. The molecular weight of the polymer product and its distribution were measured by GPC analysis. As a result, low molecular by-products were detected in a molar fraction of 0.2. The maximum temperature rise during reaction was 9°C.

Comparative Example 4:

A reaction was effected in the same manner as in Comparative Example 3 except that 188 ml of methane dichloride and 84 ml of hexane were charged into the reaction vessel. Thus, a polymer product was obtained. The reaction conditions used and the properties of the resulting polymer are altogether shown in Tables 1 and 2 below. The molecular weight of the polymer product and its distribution were measured by GPC analysis. As a result, low molecular by-products were detected in a molar fraction of 0.4. The maximum temperature rise during reaction was 10°C.

Table 1

	Solvent (charged amount (mL))	Dielectric Constant	Monomer Concentration (wt%)
Example 1	toluene (276)	2.2	24
Example 2	toluene (280)	2.2	24
Example 3	toluene (112), heptane (49)	2.2	36
Example 4	toluene (128), heptane (32)	2.2	36
Example 5	toluene (262), hexane (112)	2.2	20
Example 6	toluene (126), methylcyclohexane (54)	2.2	20
Example 7	toluene (276)	2.2	7
Example 8	toluene (276)	2.2	7
Example 9	toluene (248), hexane (28)	2.2	8
Example 10	methylene chloride (84), hexane (196)	4.6	7
Example 11	methylene chloride (56), hexane (224)	3.9	8
Example 12	methylene chloride (112), hexane (168)	5.0	7
Comparative Example 1	hexane (276)	1.9	9
Comparative Example 2	methylene chloride (28), hexane (252)	3.0	8
Comparative Example 3	methylene chloride (168), hexane (112)	6.3	6
Comparative Example 4	methylene chloride (196), hexane (84)	6.7	6

It can be seen from the results shown in Table 1 that Examples 1 to 9, wherein an aprotic solvent free of halogenated hydrocarbon was used as a polymerization solvent, exhibit a dielectric constant of from not less than 2.0 to not more than 4.0. It can also be seen that Examples 10 to 13, wherein a solvent containing halogenated hydrocarbon was used, exhibit a dielectric constant of from not less than 3.5 to not more than 5.5.

Table 2

	GPC		NMR		
	Mn	Mw/Mn	Fn(C=C) ¹⁾	Fn(indanyl) ²⁾	Mn(cal.)
Example 1	16,000	1.13	-	0.16	-
Example 2	7,200	1.24	1.95	0.0	9,100
Example 3	7,700	1.36	2.09	0.0	8,700
Example 4	7,900	1.32	2.02	0.0	8,800
Example 5	16,700	1.27	1.84	0.0	19,500
Example 6	8,800	1.37	1.90	0.0	9,600
Example 7	14,600	1.12	-	0.17	-
Example 8	14,300	1.2	-	0.18	-
Example 9	16,100	1.10	-	0.14	-
Example 10	18,500	1.07	-	0.11	-
Example 11	15,800	1.08	-	0.13	-
Example 12	18,500	1.2	1.79	0.17	-
Comparative Example 1	1,550	7.02	-	0.87	-
Comparative Example 2	2,060	7.44	-	0.60	-
Comparative Example 3	9,310	1.75	-	0.21	-
Comparative Example 4	9,270	1.6	-	0.26	-

Note

1) Average by number of carbon-carbon double bonds contained in one molecule of isobutene polymer

2) Average by number of indanyl groups contained in one molecule of isobutene polymer

The results in Table 2 show that a solvent system having a high monomer concentration free of halogenated hydrocarbon can provide an isobutene polymer having a low Mw/Mn ratio and a high terminal functionality. It can be also seen from the results of Comparative Example 1 that a solvent system comprising hexane alone cannot provide a good polymer.

INDUSTRIAL APPLICABILITY:

(1) By selecting a specific solvent system, it is made possible to prevent the resulting polymer from being precipitated and enhance the monomer concentration during polymerization.

(2) By selecting a specific solvent system, it is made possible to obtain a good polymer having a small molecular weight distribution and a small number of indanyl groups.

(3) If a solvent free of halogenated hydrocarbon is used, no special treatments for halogenated hydrocarbon in waste water or waste solvent generated from the catalyst deactivation and rinsing process after polymerization reaction are required.

Claims

1. A process for preparing an isobutene polymer having functional groups at the terminals at a temperature of from not lower than -100°C to not higher than 0°C from the following components as essential components:

(A) a cationic polymerizable monomer containing isobutene;

(B) an organic compound as an initiator/chain transfer agent represented by formula (1):



wherein X represents a halogen atom, RO- group or RCOO- group (in which R represents a monovalent organic group); R³ represents a polyvalent aromatic group or substituted or unsubstituted polyvalent aliphatic hydrocarbon group; R¹ and R² may be the same or different and each represent a hydrogen atom or substituted or unsubstituted monovalent hydrocarbon group, with the proviso that when R³ is a polyvalent aliphatic hydrocarbon group, one of R¹ and R² is not a hydrogen atom; and n represents an integer of from 1 to 6;

(C) an aprotic solvent free of halogenated hydrocarbon; and
(D) a Lewis acid,

wherein said component (C) exhibits a dielectric constant of from not less than 2.0 to not more than 4.0 at a temperature of 20°C.

2. A process for preparing an isobutene polymer having functional groups at the terminals at a temperature of from not lower than -100°C to not higher than 0°C from the following components as essential components:

(A) a cationic polymerizable monomer containing isobutene;

(B) an organic compound as an initiator/chain transfer agent represented by formula (1):



wherein X represents a halogen atom, RO- group or RCOO- group (in which R represents a monovalent organic group); R³ represents a polyvalent aromatic group or substituted or unsubstituted polyvalent aliphatic hydrocarbon group; R¹ and R² may be the same or different and each represent a hydrogen atom or substituted or unsubstituted monovalent hydrocarbon group, with the proviso that when R³ is a polyvalent aliphatic hydrocarbon group, one of R¹ and R² is not a hydrogen atom; and n represents an integer of from 1 to 6;

(C) an aprotic solvent containing halogenated hydrocarbon; and
(D) a Lewis acid,

wherein said component (C) exhibits a dielectric constant of from not less than 3.5 to not more than 5.5 at a temperature of 20°C.

3. The process for preparing an isobutene polymer terminated by functional groups according to Claim 1 or 2, wherein said component (C) contains an aromatic hydrocarbon.
4. The process for preparing an isobutene polymer terminated by functional groups according to any one of Claims 1 to 3, wherein said component (C) is a mixture of an aromatic hydrocarbon and an aliphatic hydrocarbon.
5. The process for preparing an isobutene polymer terminated by functional groups according to any one of Claims 1, 3 and 4, wherein said component (C) exhibits a dielectric constant of from not less than 2.0 to not more than 2.5 at a temperature of 20°C.
6. The process for preparing an isobutene polymer terminated by functional groups according to any one of Claims 3 to 5, wherein said aromatic hydrocarbon is selected from the group consisting of benzene, toluene, xylene and ethylbenzene.

7. The process for preparing an isobutene polymer terminated by functional groups according to any one of Claims 1 to 6, wherein the concentration of said component (A) in the system is from 5 to 40 wt%.
- 5 8. The process for preparing an isobutene polymer terminated by functional groups according to any one of Claims 1 to 7, wherein said component (B) is selected from the group consisting of p-dicumyl chloride, m-dicumyl chloride, p-dicumyl methoxide, m-dicumyl methoxide, 1,3,5-tricumyl chloride and 1,3,5-tricumyl methoxide.
9. The process for preparing an isobutene polymer terminated by functional groups according to any one of Claims 1 to 8, wherein said component (D) is boron trichloride or titanium tetrachloride.
- 10 10. The process for preparing an isobutene polymer terminated by functional groups according to any one of Claims 1 to 9, wherein an electron donor is further added as a component (E) in addition to said components (A) to (D).
11. A process for preparing an isobutene polymer having carbon-carbon double bonds at the terminals, which comprises
15 adding an allyl trimethylsilane in an amount of from 0.5 to 1.5 mol per mol of the group X in said component (B) before the formation of an isobutene polymer terminated by functional groups according to any one of Claims 1 to 10 or before the deactivation of said component (D) following the formation of said isobutene polymer.
12. A process for preparing an isobutene polymer having carbon-carbon double bonds at the terminals, which comprises
20 adding 1,9-decadiene in an amount of from 1.5 to 10.0 mol per mol of the group X in said component (B) before the formation of an isobutene polymer terminated by functional groups according to any one of Claims 1 to 10 or before the deactivation of said component (D) following the formation of said isobutene polymer.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/01164

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ C08F2/06, C08F2/38, C08F10/10, C08F4/00, C08F8/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ C08F2/00-2/60, C08F10/00-10/14, C08F4/00-4/82,
C08F8/00-8/50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 63-205305, A (Kanegafuchi Chemical Industry Co., Ltd.), August 24, 1988 (24. 08. 88), Claim (Family: none)	1 - 12
X	JP, 2-36204, A (Kanegafuchi Chemical Industry, Co., Ltd.), February 6, 1990 (06. 02. 90), Claim (Family: none)	1 - 12
E	JP, 2-245004, A (Kanegafuchi Chemical Industry, Co., Ltd.), September 28, 1990 (28. 09. 90), Claim (Family: none)	1 - 12

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

August 1, 1995 (01. 08. 95)

Date of mailing of the international search report

September 5, 1995 (05. 09. 95)

Name and mailing address of the ISA/

Japanese Patent Office

Facsimile No.

Authorized officer

Telephone No.